



## **Electrochemical surface immobilization triggers intramolecular electron transfer in multi-centre redox metalloproteins: The di-heme protein cytochrome c4**

**Chi, Qijin; Nazmudtinov, R.R; Bronshtein, M.D.; Zinkicheva, T.T.; Zhang, Jingdong; Ulstrup, Jens**

*Publication date:*  
2012

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*

Chi, Q., Nazmudtinov, R. R., Bronshtein, M. D., Zinkicheva, T. T., Zhang, J., & Ulstrup, J. (2012). *Electrochemical surface immobilization triggers intramolecular electron transfer in multi-centre redox metalloproteins: The di-heme protein cytochrome c4*. Abstract from 63rd Annual Meeting of the International Society of Electrochemistry, Prague, Czech Republic.

---

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# Electrochemical surface immobilization triggers intramolecular electron transfer in multi-centre redox metalloproteins: The di-heme protein cytochrome $c_4$

Q. Chi<sup>1\*</sup>, R.R. Nazmudtinov<sup>2\*</sup>, M.D. Bronshtein<sup>2</sup>, T.T. Zinkicheva<sup>2</sup>, J. Zhang<sup>1</sup> and J. Ulstrup<sup>1\*</sup>

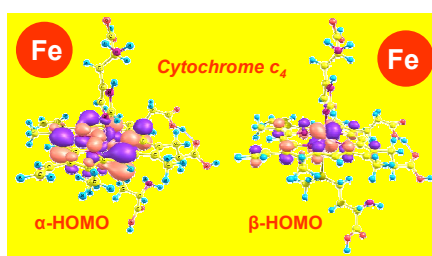
<sup>1</sup>Dept of Chemistry, Techn. University of Denmark, DK-2800 Kgs. Lyngby, Denmark

<sup>2</sup> Kazan National Research Technol. Univ., Kazan, Tatarstan, Russian Federation.

(E-mails: [\\*cq@kemi.dtu.dk](mailto:*cq@kemi.dtu.dk); [\\*nazmutdi@mail.ru](mailto:*nazmutdi@mail.ru); [\\*ju@kemi.dtu.dk](mailto:*ju@kemi.dtu.dk))

Protein film and monolayer voltammetry is a powerful tool for mechanistic redox enzyme mapping. A common observation is that composite multi-centre enzymes, e.g. copper oxidases do not themselves give voltammetric signals. Addition of substrate molecules ( $O_2$ ,  $NO_2^-$  etc.), however, triggers strong electrocatalytic signals, still caused by the enzyme, indicating that crucial changes in the enzyme molecules occur on substrate binding or surface immobilization. The di-heme metalloprotein cyt  $c_4$  (*P. stutzeri*) has emerged as a prototype multi-centre metalloprotein that offers clues to these observations. Electron transfer (ET) behaviour of cyt  $c_4$  in homogeneous solution shows clearly that ET between the heme groups is slow. Immobilization on well-defined SAM-modified Au(111)-electrodes, however, open efficient intramolecular ET channels, clearly displayed by the two-ET voltammetric cyt  $c_4$  behaviour.

We present here a comprehensive experimental and theoretical (quantum chemical) analysis of the intramolecular ET behaviour of cyt  $c_4$  in bulk solution and on a SAM-modified electrochemical surface. The electronic coupling between the heme groups is, particularly, exceedingly sensitive to the conformational environment and increases by many orders of magnitude on even tiny, thermally accessible structural fluctuations. Low-energy conformational triggering of electronically based facile ET channels therefore offer a clue to broadly observed metalloenzyme voltammetry.



## Two references:

1. Q. Chi, Q., J. Zhang, T. Arslan, L. Borg, G.W. Pedersen, H.E.M. Christensen, R.R. Nazmudtinov, J. Ulstrup, *J. Phys. Chem. B*, 2010, **114**, 5617-5624.
2. R. R. Nazmudtinov, M.D. Bronshtein, T.T. Zinkicheva, Q. Chi, J. Zhang, J. Ulstrup, *PCCP* (2012), in press.